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THE UNIVERSITY OF ALBERTA

Chemical Analysis of Bone Material as an Aid to the
Discernment of Horizontal Stratigraphy

by

(C) Walter Anthony Kowal

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF Master of Arts

Department of Anthropology

EDMONTON, ALBERTA

SPRING 1986

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled Chemical Analysis of Bone Material as an Aid to the Discernment of Horizontal Stratigraphy submitted by Walter Anthony Kowal in partial fulfilment of the requirements for the degree of Master of Arts.

.....
Supervisor
.....
.....

Date... 21 October 1985

This manuscript is dedicated to my mother for all her
love and understanding

Abstract

Large Arctic multi-component surface sites present problems for archaeological interpretation due to their unique polar desert environments. Materials deposited on the site surface are not subjected to the usual forces of weathering and sedimentation so horizontal stratigraphy or spatio-temporal developmental scheduling becomes difficult to evaluate.

To help evaluate a suspected developmental scheme at site PjRa-18 (the Kuptana Site), Banks Island, N.W.T., muskoxen bone is analyzed. It is argued that differential chemical alteration of bone parent material can be used to gauge the length of exposure to the forces of weathering. Electron probe microanalysis and radio-frequency inductively coupled argon plasma atomic emission spectroscopy (RF-ICAP-AES) are utilized to ascertain elemental concentration levels in bone from within four areas of the site.

The electron microprobe proves to be of little value for bone analysis at the minor or trace levels due to the volatility of organic components within the bone matrix. Conversely, RF-ICAP-AES is of great utility in providing information on the elemental composition of bone at the major, minor, and trace levels. Both wet and dry oxidation-reduction procedures are utilized in this study and demonstrate a high degree of conformity. Assessment of the resultant data indicates that bones from four areas of

the site are chemically dissimilar. In terms of the horizontal stratigraphic profile postulated for the site, bones from the area thought to be the oldest showed the most chemical alteration, that is, loss of parent material.

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Before I can acknowledge any individuals for their contributions to the fulfillment of this research endeavour, I must first express my utmost gratitude, thanks, and appreciation to the Boreal Institute For Northern Studies, University of Alberta, for their generous support which enabled this research to be initiated and completed.

Also, the one individual who above all others deserves to be singled out for his contribution, support, and involvement in this project is my thesis committee supervisor, Dr. Clifford Hickey of the Department of Anthropology, University of Alberta. Dr. Hickey showed remarkable patience and latitude by allowing me to engage in non-academic monetary pursuits for over four years even though his own research efforts were complicated by this delay. For this he deserves even greater thanks and an apology. At this stage I would also like to thank the other members of my committee, Dr. Owen Beattie of the Department of Anthropology, University of Alberta, and Dr. Peter Krahn, Director, Occupational Health and Safety Division, Laboratory Services Branch, Alberta Workers' Health, Safety and Compensation, for the confidence they showed in me and this experimental research.

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I. Introduction

In this thesis I will examine modern and archaeological faunal material using relatively new analytical techniques for compositional analysis. This study was undertaken to ascertain whether these compositional analysis techniques could be of utility in the analysis of archaeological faunal materials.

The contained experiments were not undertaken with the goal in mind of supplanting conventional faunal analysis techniques, but rather to augment and supplement them by providing new data heretofore unobtainable using existing techniques. The experiments in fact utilize conventional macroscopic and microscopic methods to establish the data base to which compositional analysis results could be correlated.

This chapter will provide information on two topics, thereby serving as an introduction to the main body of the thesis. The first subject is a brief and general overview of the Copper Inuit occupation of Banks Island, N.W.T., during the late nineteenth century; the second is a discussion of the direction taken by this particular research, within the context of the archaeological problems relating to this occupation.

The faunal material utilized in this study was collected from Site PjRa-18, Banks Island, N.W.T. Banks Island, the southwesternmost island of the Canadian Arctic Archipelago (Fig. 1), is located between 71 and 75 degrees

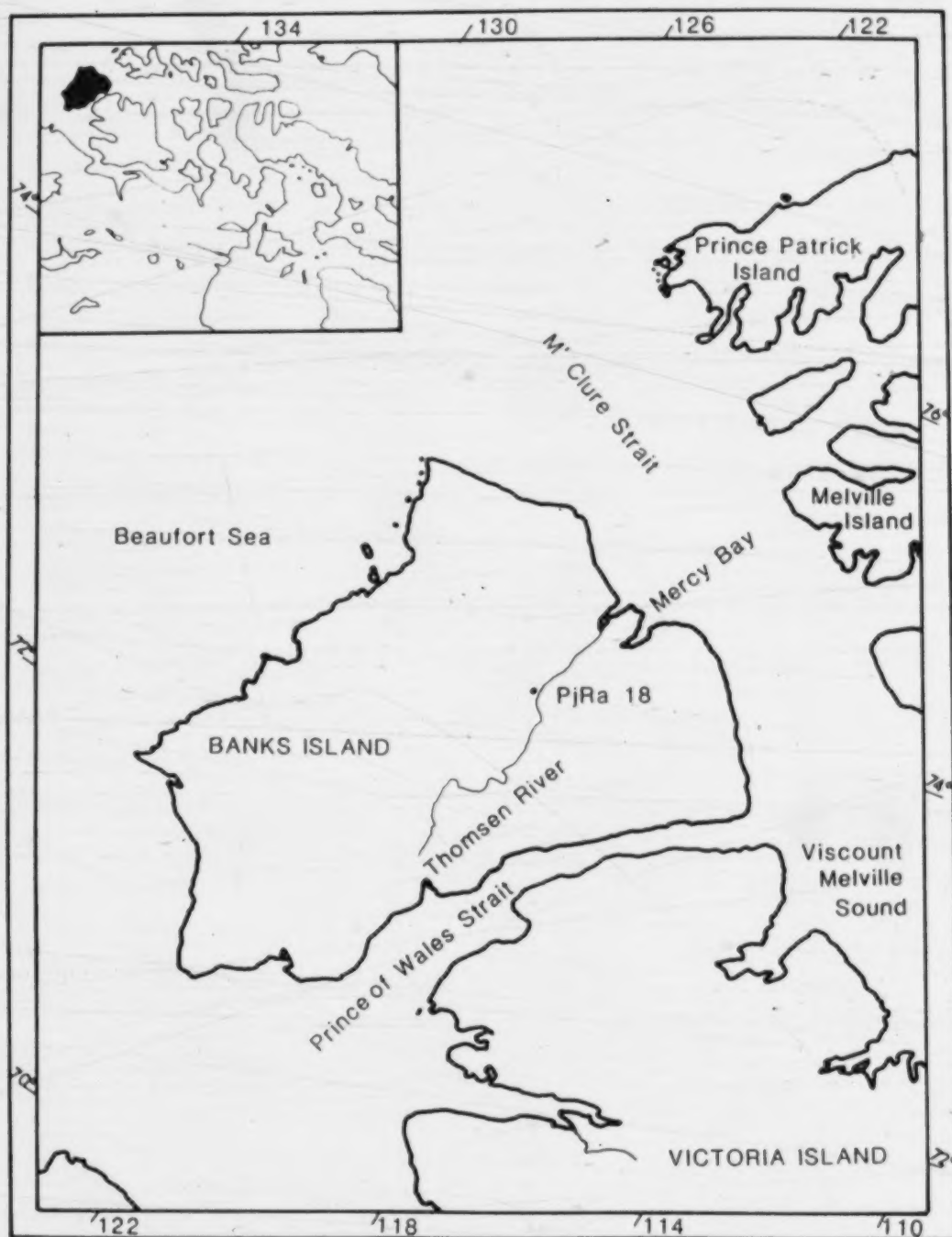


Figure 1: Site Location Map

north latitude and 115 and 126 degrees west longitude. The island is approximately 400 kilometers long and ranges from 200 to 320 kilometers in width, encompassing an area of 60,165 square kilometers (Vincent, 1982).

Historical and Archaeological Background

Banks Island's geographical location and large size account for its historical importance as it lies athwart the western entrances to the various northwest passage routes (Usher 1966). Although Banks Island had been occupied at various periods during pre-Dorset and Thule times (Manning, 1956; Taylor, 1955; Arnold, 1981), there is no evidence to suggest that any but a small portion of it was occupied when first discovered and mapped by British expeditions in the first half of the nineteenth century (Osborn, 1895; Collinson, 1889). Ethnographic evidence gathered by Stefansson (1913, 1921) suggests that it was the abandonment of the Franklin Search Expedition vessel, H.M.S. Investigator in 1854 at Mercy Bay (northeastern Banks Island) that precipitated the reoccupation of Banks Island during the latter half of the nineteenth century.

Stefansson concluded that Inuit from Victoria Island discovered the abandoned ship and/or its cache of stores shortly after 1855. Moreover, Stefansson suggested that the Inuit were drawn back to the area on many subsequent occasions for the purpose of obtaining the large quantities of European goods that represented untold 'wealth' to the

resource limited Inuit. Stefansson estimated that over 1000 Inuit had visited the area over a thirty year period, with the last visits occurring around 1890 (1921: 240-241).

In an attempt to ascertain the effects of the large influx of goods on nineteenth century Copper Inuit culture, Dr. Clifford Hickey, of the University of Alberta, has been conducting archaeological investigations on both Banks and Victoria Islands, as well as studies of Copper Inuit artifact collections in various museums, published and unpublished historical records, and conducting ethnohistorical research at the communities of Sachs Harbour and Holman Island (Hickey, 1984). The first phase of his 'Copper Inuit Research Project' was to delimit and characterize the nineteenth century occupation of Banks Island. The primary aspects of this work included:

"assessing the kinds and amount of exotic materials available to and utilized by the Copper Inuit; determining the material and other effects of this incorporation; defining subsistence relationships between the Inuit and prey; and reconstructing settlement and scheduling strategies (including seasonality of various activities, and frequency and duration of occupation of various sites)" (Hickey, 1982).

By the beginning of the 1980 field season, around 115 nineteenth century Copper Inuit sites had been located on Banks Island, and another 80 would be found in 1981 and 1982. One of these, site PjRa-18 (Fig. 2), was chosen for intensive testing in 1980 because a preliminary survey of the site by Hickey in 1978 indicated that it might yield specific information regarding most aspects of the first

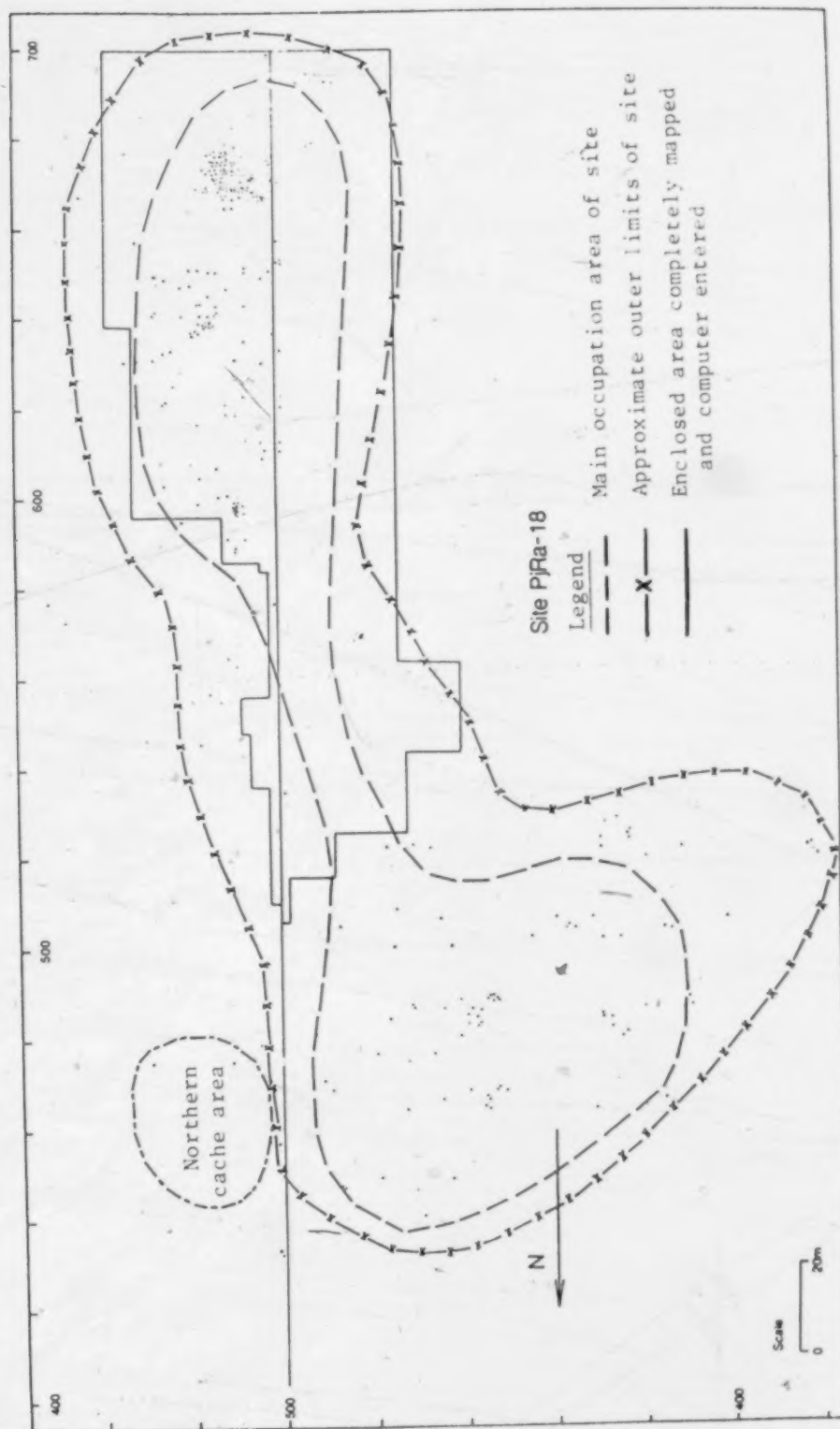


Figure 2: Distribution of Muskoxen Skulls on Site PjRa-18

phase of the above research project.

PjRa-18 (the Kuptana Site) has been defined by Hickey as a large multi-component surface site, covering an area between 17,000 and 20,000 square meters. On the basis of Stefansson's work the site may have been occupied at various times over a period of thirty years (Stefansson, 1913, 1921). The site was extensively mapped and excavated during the 1980, 1981, and 1982 field seasons and interpretation of the resultant data has been proceeding along essentially standard archaeological lines.

Prior to the start of the 1980 field season Hickey was aware that problems would be encountered in the interpretation of site development. A preliminary analysis of artifact clustering made it clear that there were distinct components to the site that could be designated living areas and processing areas.

A few areas were hypothesized to have been utilized repeatedly on the basis of superposition of artifacts and architectural features, but the major obstacle in the reconstruction of site development was the vast quantity of faunal remains in the southern section of the main part of the site. In particular, it was not possible to distinguish chronologically discrete sub-units. It was therefore not possible to ascertain the frequency of occupation of the site, nor the extent of occupation at any particular time. Some suspected developmental scheduling has been postulated and it is to these suspected but unconfirmed sequential

developmental schemes that the analyses contained in this study are focused.

Focus Of The Thesis

This study attempts to evaluate methods that could be used to unravel the internal chronology of large Arctic multi-component surface sites. These sites developed and survive under conditions unique to polar desert environments. Cold temperatures and snow-cover for much of the year act to protect culturally deposited materials from the effects of normal weathering and destruction. Artifacts once deposited on the site surface remain relatively unchanged for many years and because there is little sedimentation it is often impossible to identify the sequence of artifact deposition or to utilize such procedures as searching for differential deterioration of bone artifacts. Therefore the developmental sequence or "internal chronology" of the site is often obscured or erased. The compositional analyses employed in the present study were initially undertaken to ascertain whether observable differences in bone chemical composition could be detected in bones from different areas of the site. My primary assumption is that bone undergoes matrix loss with time due to ion loss and exchange. That is, given chemical leaching primarily through water percolation, ceteris paribus, older bone material should contain less of the primary constituent elements than recent bone. Therefore, if

a site had taken a number of years to develop, it is reasoned that the bones from the earliest areas occupied should have lost more of their constituent elements than should the bones from the areas of more recent occupation.

I propose that the loss of mineral material can be used to determine length of exposure to the processes of weathering. To test this hypothesis, two chemical analysis techniques were utilized (described below). The present study is a preliminary work where new formalized procedures and reference data had to be developed. As such the study utilized two chemical analytical techniques in an attempt to derive specific information for the interpretation of Arctic archaeological site developmental sequences.

Since the Copper Inuit material under investigation is assignable to a narrow time frame, investigations regarding chronology were doubly difficult. Even though the bone material could be anywhere from 90 to 125 years old (Stefansson, 1921), the amount of significant physical weathering was confined to the short Arctic summer months when the bones were not frozen or snow covered. Therefore, most active bone degeneration would occur only during two or three months of each year.

Normally, bone on the surface of a site is broken down when collagen is attacked by the bacterium Clostridium histolyticum (Rottländer, 1976), but this bacterial action is slowed or eliminated in cold or very dry climates. Since Banks Island lies within a polar desert environment

(Maxwell, 1981), this bacterial action is probably not significant. Factors which have a bearing on bone decay are water percolation, air exposure, temperature oscillations (resulting in exfoliation), exposure to sunlight (particularly ultra-violet rays), lichen growth on bone surfaces, erosion from wind borne particles, and movement within bone caused by thermal action. But, the main agent of bone weathering at site PjRa-18 is believed to be water percolating through the bone. As Northeastern Banks Island receives less than 25 centimeters of precipitation each year (Maxwell, 1981), with most of this occurring as rainfall during the summer months, the actual amount of bone disintegration would be expected to be slight. Visual examination of the bone material on the site supported this conclusion.

Given these conditions for bone preservation, the amount of elemental concentrations between bones from within a narrow time period should be slight. The experiments initiated below try to evaluate these differences within the context specified above.

II. The Nature Of Bone

While it is not the intent of this chapter to examine all aspects of bone growth, development and general morphology, it is necessary to examine in some detail those aspects that had a direct bearing on the current research: that is, why it was initiated, the direction it took, and the subsequent conclusions obtained from the derived data.

The major obstacle to experimental analysis is the general biophysical design of bone and the nature of bone material. Mammalian bone presents problems for analysis because it is a living tissue capable of altering its properties and configuration in response to variations in nutrient supply and/or mechanical demand. Calcified tissue (bone and teeth) consists of both an organic fraction and inorganic fraction (Oldroyd and Herring, 1968). The organic fraction is composed of two components, the cells and the intercellular substance. The inorganic fraction is composed of crystals of inorganic salts which have the basic structure of an apatite.

Living bone has three types of cells: osteoblasts, osteoclasts and osteocytes which have distinct but probably overlapping functions (Engfeldt, 1958). Osteoblasts participate in the formation of the bone matrix. Osteoblasts are found covering newly formed bone structures and arrange themselves in continuous layers. Osteoclasts are involved with bone resorption or destruction. Osteocytes, the most abundant cells, are osteoblasts that have become surrounded

by intercellular substance and are necessary for maintaining the structure and function of the fully developed bone tissue (Matter and Siegel, 1979).

The intercellular substance of the organic matrix is comprised of collagen fibers and polymerized glycoproteins to which the mineral salts, mainly calcium phosphates, are bound (Weinmann and Sicher, 1955). The inorganic fraction of bone consists of microcrystals of calcium phosphate which has the basic structure of hydroxyapatite. No single formula can be given for bone mineral because there can be at least five different calcium phosphate compounds within bone at any one time, these are: dicalcium phosphate dihydrate, octacalcium phosphate, amorphous calcium phosphate, tricalcium phosphate and hydroxyapatite.

The various calcium phosphate compounds share features with the others in the series so that structural planes may be identical, thus the Ca/P ratio may vary but the lattice structure is preserved. In bone there is a two-way chemical transference between the bloodstream and the cells and matrix in a regulated steady state disequilibrium (Neuman, 1980). This steady state disequilibrium ensures that the mineral phase of bone retains chemical flexibility and susceptibility to regulation by cellular activity. Non-equilibrium boundary conditions ensure that chemical composition varies not only from one bone to another but also within the microstructures of the same bone. If the mineral phase of bone was locked into a fixed solubility

equilibrium with blood serum, modifications in dietary intake would allow alternations between hypocalcemia and hypercalcemia.

Since the extracellular fluids are enormously complex, bone mineral forms in a medium containing many more ions and substances than simply Ca^{++} , P, or OH^- . Consequently, a variety of elements other than the classical constituents of hydroxyapatite are found in bone. Particular ions may substitute for certain constituents of the crystal lattice itself, while others are only adsorbed on the surface of the crystal or in the outer hydration shell. Among the prominent elements that may substitute within the crystal lattice are Sr^{++} and Pb^{++} for Ca^{++} ; F^- for OH^- and CO_3^{--} for PO_4^{--} (Tipton and Cook, 1963; Tipton and Shafer, 1964; Tipton et al. 1965; Becker et al. 1968).

At the surface of the crystals spatial and charge requirements are less restrictive allowing for a greater number of possible ion substitutions. Mg^{++} , Sr^{++} , Ra^{++} , Pb^{++} , and Na^{++} can substitute for Ca^{++} and CO_3^{--} , citrate, phosphate esters, pyrophosphate and amino acids for phosphate (Neuman, 1980).

The extracellular fluid can contain up to 50 different elements which can be incorporated into bone tissue. Bone acts as a repository for many of the body's ions with exchange occurring during bone formation and resorption. Movement of ions in and out of bone is greatly affected by the content of the extracellular fluid which is greatly

affected by diet, but may also be dependent on such factors as animal age or sex, and variation between species (Vaughan, 1981).

Hydroxyapatite crystals are no larger than $500 \times 200 \times 100$ angstroms so that an enormous surface area is exposed. The total bone crystal surface in man for example has been estimated to be 300 square meters per gram (Matter and Siegel, 1979). Though much of this crystal is inaccessible for exchange with blood-borne ions, at least several per cent of the bone mineral is in equilibrium with the extracellular fluid, providing an ion exchange surface of enormous capacity and reactivity (Neuman and Neuman, 1958).

There are two main types of bone: coarse fibrillar bone of an immature type and fine fibrillar or lamellar bone (Engfeldt, 1958). The adult skeleton is mainly composed of lamellar bone which in turn can be subdivided into two main types, cortical bone and trabecular bone. Cortical bone is the harder, more compact bone found on the outer surfaces of all bones. Trabecular bone is the less dense inner bone which lies internal to but contiguous with compact bone. Trabecular bone consists of bars, plates or tubules of bone of varying thickness and length joined in a three-dimensional network. The single trabecula consists of a few lamellae, generally arranged parallel to each other or in concentric layers (Boyde and Hobdell, 1969). Throughout all bone are cavities and canals of varying sizes containing a variety of cells and blood vessels. In compact bone the

vascular channels are very narrow while in trabecular bone the cavities are appreciably larger and contain varying amounts of connective tissue, fat tissue, blood forming tissue, and blood vessels.

Mature bone is laid down in thin layers of intercellular substance 4 to 12 microns thick with the osteocytes spread out in the plane of the layers or lamellae. The osteocytes are in fact found between the lamellae. In lamellar bone, each lamella is separated from adjacent lamellae by a thin layer of less mineralized tissue referred to as an interlamellar cement line (Ascenzi et al., 1965). Bone grows in thickness by means of apposition of new lamellae upon the surface of existing bone tissue.

It is the appositional incrementation of lamellae that first prompted this study to investigate the possibility of using bone decay as an indicator of site development and destruction. Since it can be shown that bone disintegrates almost in the reverse order of bone formation, that is from the outer circumferential lamellae inwards (Uerpmann, 1973), I proposed that the loss of mineral material from individual lamellae could be used to determine length of exposure to the processes of weathering.

The outer circumferential lamellae are very dense and contain extremely small nutrient passages and thus are very resistant to water penetration. As water is the primary mechanism of bone weathering in surficial deposits, decay proceeds slowly at first. It is only after water penetrates

and erodes the interlamellar bonding cement that the outer compacta begins to exfoliate. Once the harder outer layers are removed the less dense inner bone is exposed to greater water penetration. Because the inner layers are porous a greater flow of water through the material ensures that the process of weathering is markedly enhanced.

In the experimental analyses (Chapter 4) I will examine a technique for dating bone on the quantities of mineral elements that are chemically leached out of the parent bone material layer by layer. If successive lamellae can be shown to demonstrate differences in chemical constituents a pattern of mineral loss may be found that can be correlated to the length of time since deposition.

To test the viability of this model it was necessary to employ a technique of analysis that could isolate and identify individual lamellae optically as well as provide analytical results on the areas under observation. As these lamellae range in thickness from four to twelve microns the method of analysis employed had to allow visual examination and chemical analysis at the micron level. Therefore it was necessary to find a technique capable of analyzing sequentially at the micron level. That is, to do a point by point transect from the outermost layer towards the central core of the bone. The only machine that offered these features was the electron microprobe. Thus, the experimental analyses described below begin with a focus on the microprobe analysis of archaeological bone.

III. Material

I began the Banks Island muskoxen bone study with few preconceptions concerning the factors that could affect the outcome of this study. Since access to the faunal material was restricted to a single season (1980) it was imperative to decide beforehand which anatomical elements were to constitute the sample material. Regard had to be made for accessibility and survivability common to all age and sex groups. A specific area of a single bone had to be selected to insure standardization and minimize the regional variations which arise from the different structural and functional demands of dissimilar bone elements. Also, for the purposes of comparison, the structure, form and function of particular bone elements affect the rate of chemisorption and depletion.

On this basis, occipital condyles were selected as being best suited for the type of analyses to be employed in this study. It was assumed that most muskoxen skulls would still possess intact condyles and these could be removed without much difficulty. Also condyles have well developed cortical and trabecular areas suitable for microanalysis.

In the event that condylar preservation was poor, the frontal bones were selected as an alternative sampling site. Though these could be removed readily, they lacked the well developed cortical and trabecular areas of the condyles and as such they were not considered as good a sampling site.

Preparatory work for my fieldwork consisted of the creation of a standardized form on which to record all the data that could affect the outcome of the projected analyses. A maximum of twenty-two discrete observations were to be made for each skull. Gross age categories were constructed to accommodate lack of control in the field as to the specific ages of individual animals. Metric measurements were taken for the calculation of indices since the large number of animals on the site could provide a core of data regarding population characteristics of this particular group of animals. Tooth eruption and wear were to be recorded to aid further in establishing the relative age of individual animals and also to provide assessment of animal age and season of death by dental annuli examination (Miller, 1974; Savelle and Beattie, 1983).

The large sample, from a wide variety of locations in the site (Fig. 2) and complete with age, sex, orientation, general condition of each specimen, orientation with respect to cardinal directions, and metric data provides a good data base from which to compare individuals against the norm, as well as against groups from discrete areas of the site. But, in order to obtain usable data archaeological materials had to be calibrated with modern referrent materials. To this end, eight modern animals, from recent kill sites near PjRa-18, were sampled. Here, too, data were collected to establish the age, sex and season of death of each animal.

The procedure followed in this study was to establish a compositional norm (or characteristic signature) for a particular class of materials, in this case modern muskoxen bone, and then to compare these to the archaeological specimens. Since the rate of post-depositional chemical alteration was to be calculated by microprobe analysis, it was necessary to ascertain the range of elements within recent unweathered bone. Since the uptake of elements within living organisms is environmentally determined, the modern sample, taken from animals from the same locality, should closely resemble the original condition of the archaeological specimens.

IV. Methods

The kind of analyses described below are not unique in their application to bone analysis as there has been a growing trend in archaeological data collection and analysis to utilize more fully the innovations and technologies developed in the physical sciences. The increasing emphasis on technology has resulted from the desire to extract more information out of the often meagre materials available.

While the relationship between archaeology and the physical sciences goes back at least to the late nineteenth century (Haering, 1975), it was the development of radiometric dating techniques in the middle of this century that had the most profound influence on strengthening this relationship (Aitken, 1961; Brill, 1971).

Radiometric dating allowed for the temporal ordering of cultural materials, and fairly extensive chronologies resulted. Once one of the primary goals of archaeology, chronology became the framework around which other research objectives were formulated. Most of these objectives concerning prehistoric technology, economy, social organization, palaeonutrition, palaeopathology, and palaeoecology can only be partially answered by traditional methods of analysis (Wing and Brown, 1979). Traditional faunal analysis, for example, proves to be of little use when faunal remains have been severely modified by post-depositional effects.

The development of various analytical methods which yield information about the elemental composition of materials appear to provide a better means to address some of the above research objectives. These include the techniques of atomic absorption spectrometry, neutron activation analysis, x-ray fluorescence and various other x-ray diffraction methods. These techniques can offer both qualitative and quantitative data, often with high levels of sensitivity.

Though most commonly used to study inorganic substances such as obsidian, flint and ceramics to determine their geographic sources by compositional differences (Gordus et al., 1968; Sieveking et al., 1970; Aspinall and Feather, 1972; Bowman et al., 1973; Banterla et al., 1973), there have been some recent studies of organic materials as well (Jervis et al., 1961; Zmijewska and Semkov, 1978; Ördögh, 1978; Kostadinov and Djingova, 1981; Kučera and de Goeji, 1981). Although few studies have been done, promising results have been obtained from the analysis of bone material (Becker et al., 1968; Lambert et al., 1979; Langmyhr and Kjuus, 1978; Gawlik et al., 1981; Hyvönen-Dabek et al., 1981; and Hyvönen-Dabek, 1981). The compositional nature of bone, and particularly its trace element aspects, have been widely studied from a number of biological science orientations (Kerr and Spyrou, 1978).

The results of recent experiments suggests that patterned relationships in the concentration of elements

within bone do exist, and that such relationships may be utilized as a basis for the investigation of problems concerning prehistoric economy, technology, palaeonutrition, social organization, and palaeoecology (Wessen, 1975; Wessen et al., 1978; Schoeninger, 1979; Beattie, 1981).

The present research was undertaken to determine if these patterned relationships could be of utility in unravelling the internal relative chronology of large Arctic multi-component surface sites. To examine the possibility of patterned matrix loss over time, two types of analysis were employed: 1) total compositional analysis and 2) discrete point analysis. Total compositional analysis was accomplished using a radio-frequency inductively coupled argon plasma atomic emission spectrometer (RF-ICAP-AES), while the electron microprobe was used for the discrete point analysis.

Total compositional analysis was undertaken to establish the range of elements within the bone samples under investigation to aid in the selection of particular elements for individual isolation studies. It seemed likely that the pertinent information from the analysis was going to be dependent on the concentrations of only a few elements or ratios of elements. The advantages of total analysis are that the results give an upper limit for the availability of an element within the sample. The disadvantages lie in the fact that there is no regional separation and there is usually no chance of reproducing the results because of

sample destruction. For this type of analysis, neutron activation, x-ray fluorescence and atomic absorption have been methods most used in archaeological investigations (Wessen, 1975; Wessen et al., 1978; Schoeninger, 1979; and Beattie, 1981). It was my intention to use one of these methods myself when I began my current research, but I was advised by a number of analytical chemists at the University of Alberta to consider the use of RF-ICAP-AES, not only as a replacement for these other techniques, but as a more viable and accurate alternative. For simplicity, the technique is generally referred to as atomic emission spectroscopy (AES) and the machine as the inductively coupled plasma (ICP). Comparisons of precision and accuracy between AES and other analytical techniques favour AES as the preferred analytical technique for the discernment of most elements at the major, minor or trace levels (Fassel and Kniseley, 1974; Winefordner et al., 1975; and Amini et al., 1981).

ICP Analysis

The ICP yields results which are generally within one standard deviation of the results of other methods and is therefore regarded as a good alternative to the more time-consuming single element methods such as atomic absorption spectroscopy. Apart from sample dissolution, no pre-treatment of the sample is required, and pure standards can be used for calibration.

Although it is not the primary intent of this study to examine fully the history and all the theoretical aspects of the plasma, the discussion that follows may prove useful to the reader unfamiliar with the field.

The principles behind the operation of the ICP are easy to understand. A plasma is a highly ionized gas which results when the atoms and molecules of a gas are thermally excited. When a gas is raised to a high temperature (between 4000 and 10,000 degrees K), the atoms and molecules of the gas are highly excited, precipitating violent collisions of particles which result in the stripping-off of electrons. These electrons cause collisions with the gas atoms and produce still more free electrons. The increased number of free ions and electrons affect the dynamical behaviour of the gas and its properties are sufficiently different from those of a normal non-ionized gas to be called a plasma (Greenfield et al., 1976).

A fine spray of solution taken from the sample tube to be analysed is injected into the plasma flame. Because it is a solution spray it is a representative portion of each sample and assures its uniform distribution throughout the body of the plasma flame (Fig. 3). These atoms and molecules are raised to an excited electronic state through thermal collisions with the constituents of the plasma gas, and when they return to a lower or "ground" electronic state they emit light whose wavelengths are characteristic for each element within it, with an intensity directly proportional

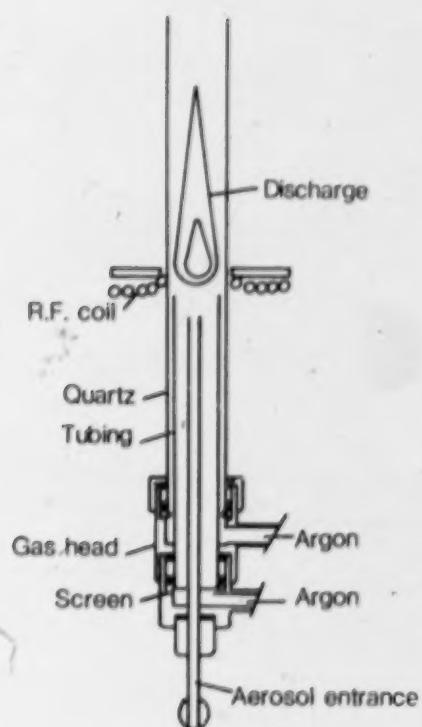


Figure 3: Schematic diagram of Plasma Torch.

to the element's concentration.

This light is focused by a collimating lens onto the entrance slit of the spectrometer (Fig. 4). It passes the entrance slit and illuminates a diffraction grating. At this point the light is polychromatic and is characteristic of all elements in the excited sample. The light is diffracted by the grating and is separated into its component wavelengths to form a spectrum. The photons of the spectral lines are registered by photomultiplier tubes, and the output is amplified and displayed on a digital readout.

The number of elements that are determined simultaneously is dependent on the number of elements the machine is set up to analyze, and is determined by the number of photo-multiplier tubes present. Newer machines have the capability of analyzing up to 60 elements. The ICP can be used for most elements, especially the metals. It cannot distinguish isotopes, nor can it do some gaseous elements like hydrogen and oxygen because pure elemental hydrogen or oxygen would explode in the plasma flame.

The ICP analysis for this study was done at Chemical and Geological Laboratories (Ltd.) in Edmonton, Alberta. The instrument used was the Jarrell-Ash Plasma AtomComp Model 9000 equipped with an ICP unit (Fig. 5). The system was controlled using an Apple II micro-computer as the dedicated controller. The Jarrell-Ash Sample Analytical Task Program (version 3.1) provided the software commands to control spectrometer functions. The ICP was calibrated using a

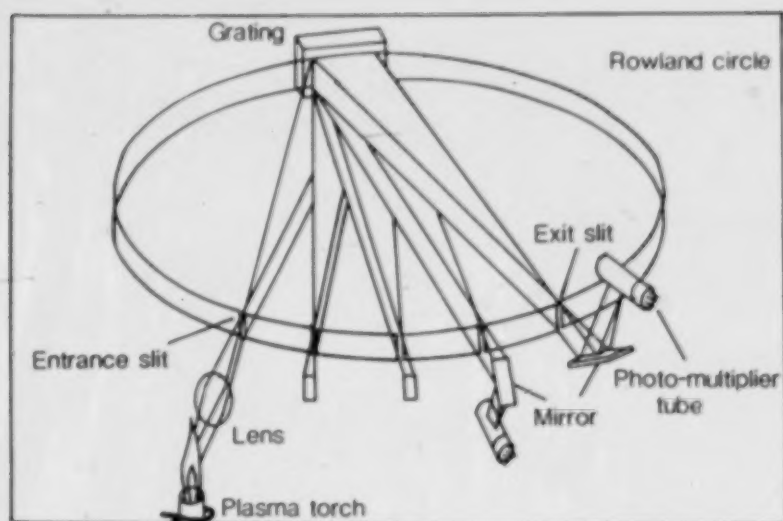


Figure 4: Schematic diagram of an ICP Spectrometer

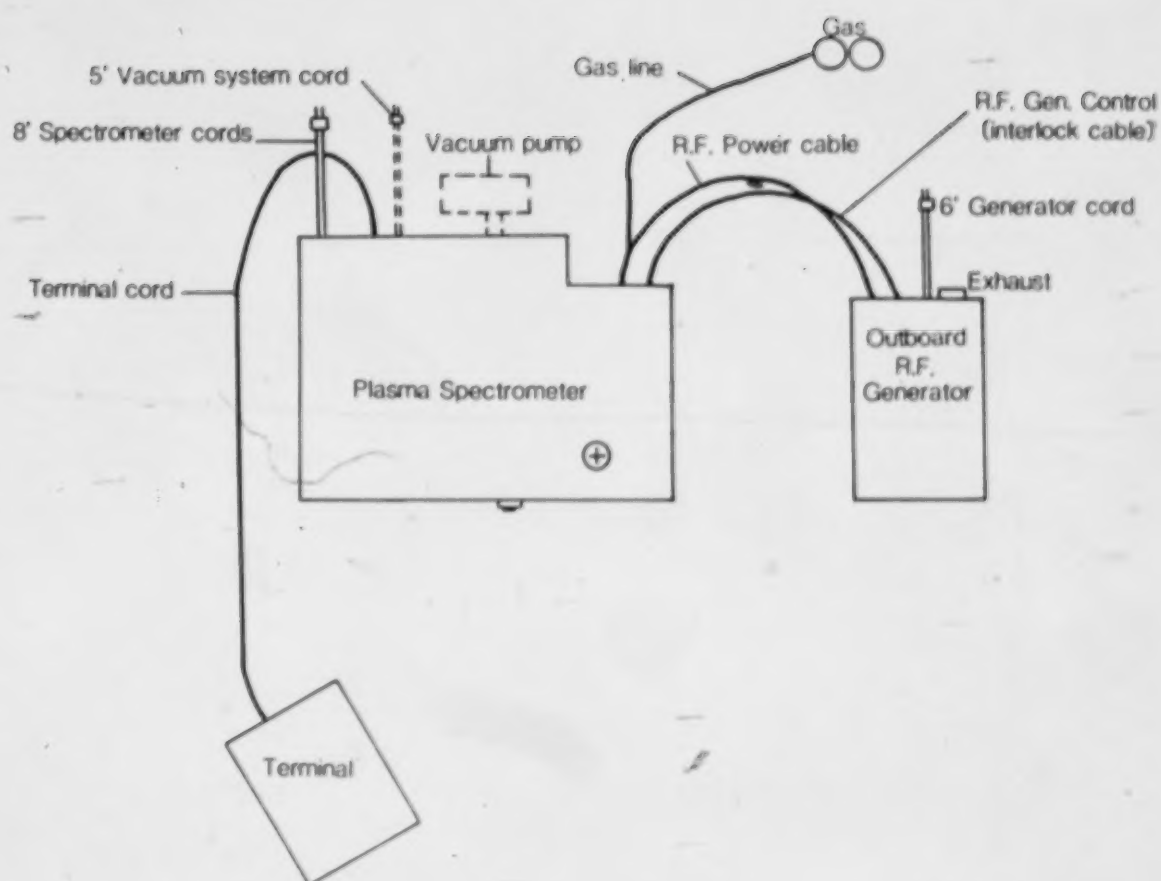


Figure 5: Schematic diagram of the Jarrell-Ash Plasma Atom-Comp Model 9000

mercury lamp profile. The 9000 was set to analyze 26 elements (Table 1). The spectral lines that were read are also listed in Table 1.

This particular machine provided for the simultaneous determination of 26 elements, ranging from lithium of atomic number 3 to lead of atomic number 82. Since this was a machine used for commercial purposes, these elements represented those that are most commonly requested in the various analyses normally undertaken by the laboratory.

For ICP analysis 13 samples from five recent kills were selected (Table 2). The animals were sexed by visual clues based on horn core growth, development and robusticity. The sample population consisted of one adult male, one adult female, a subadult male, a subadult female, and a young juvenile of indeterminate sex.

Sample preparation was minimal. The samples were washed in distilled water and oven dried at 105 degrees celsius for four hours. One gram was taken of each sample and dissolved in concentrated reagent grade nitric acid then diluted to 100 ml using distilled water. The dissolution process required the application of some heat and was completed in about four days.

Electron Microprobe Analysis

Discrete point analysis was performed using the electron microprobe facilities in the Geology Department at the University of Alberta. These facilities are supported in

Table 1: Elements Analyzed By The ICP

Element	Atomic Number	Spectral Line Read
Ag	47	3382
Al	13	3093
B	5	2497
Ba	56	4554
Be	4	3130
Ca	20	3179
Cd	48	2265
Co	27	2286
Cr	24	2677
Cu	29	3247
Fe	26	2599
K	19	4047
Li	3	6707
Mg	12	3832
Mn	25	2576
Mo	42	2020
Na	11	3303
Ni	28	2316 X 2
P	15	2149 X 2
Pb	82	2203
Si	14	2881
Sr	38	4077
Te	52	2142
Ti	22	3349
V	23	2924
Zn	30	2138 X 2

Table 2: Bone Samples Used For Plasma Analysis

Number	Animal	Anatomical Element
1	379 - Adult Female	Right Condyle
2	379 - Adult Female	Rib
3	379 - Adult Female	Femur
4	379 - Adult Female	Premaxilla
5	379 - Adult Female	Mandible
6	384 - Adult Male	Right Condyle
7	384 - Adult Male	Femur
8	384 - Adult Male	Rib
9	384 - Adult Male	Mandible
10	384 - Adult Male	Innominate
11	382 - Subadult Male	Right Condyle
12	378 - Subadult Female	Right Condyle
13	383 - Indeterminate Immature	Right Condyle

part by NSERC Grant A4254 to D.G.W. Smith.

The instrument used was an Applied Research Laboratories "SEMQ" electron microprobe fitted with an Ortec EEDS II energy dispersive system. It was operated at 15 KV with a probe current of about 5 nano amps. The instrument uses a 1024 channel-multichannel analyzer displaying 0-10.23 KEV integrated photon counts. The region from channel 185 to channel 218 inclusive was used for P K alpha radiation. The region from channel 353 to channel 417 inclusive was used for integration of Ca K alpha and K beta.

An electron beam is focused on a small area (≈ 1 micron²) on the surface of the sample material (Fig. 6). X-rays characteristic of the constituent elements are excited within the microvolume penetrated by the electrons and are radiated out of the sample. The wavelength (or energy) of the x-ray photons are characteristic for each of the constituent elements in the sample with the intensity of the emissions being dependent on the concentration of the elements present. X-rays which are emitted from the target sample are dispersed by a movable diffracting crystal. By rotating the crystal to precise angles an x-ray image of the x-ray source can be focused on the x-ray detector.

To see the point of impact of the probe beam the microprobe is equipped with an optical microscope capable of magnifications up to 300X. For further precision a beam from a cathode ray tube is moved synchronously with the probe beam so that as a signal is produced as a consequence of the

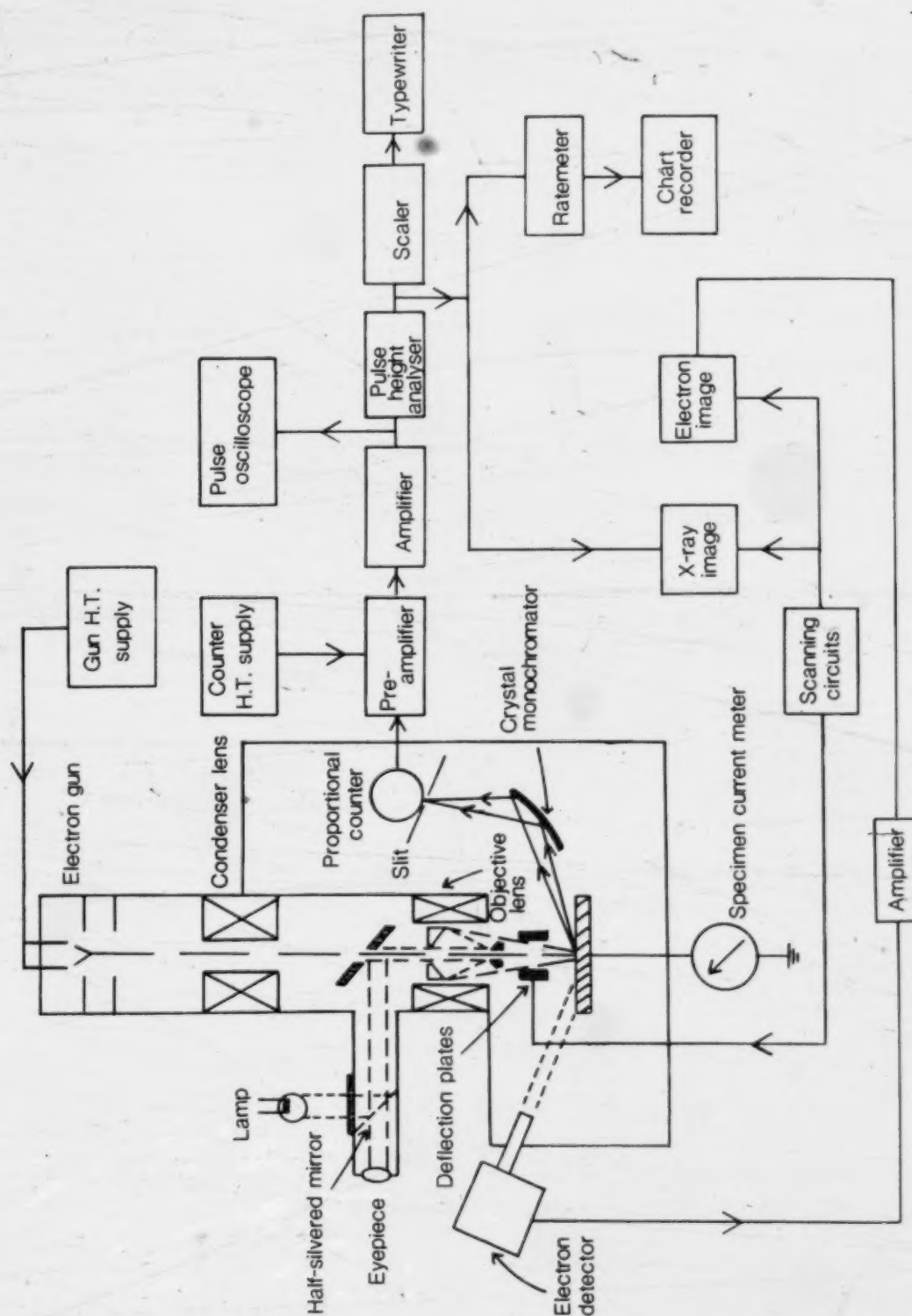


Figure 6: Schematic diagram of an Electron Probe Microanalyzer

electron beam interacting with the sample an electron image is produced in the form of a bright spot at the position on the screen corresponding to the point on the sample where the photon originated. In this way the beam can be controlled by the operator and directed with reference to this image. A more detailed description of microbeam techniques, analysis and instrumentation can be found in Smith (1977).

In microprobe analysis the sample must be placed in a vacuum to prevent attenuation of elements in air. Since the microprobe operates on the principle of positive and negative potentials it is necessary to coat samples with carbon to make them conductive to electrical charges. The carbon coating also makes the samples more resistant to heat, which is critical since volatile materials may emit undesirable substances which could coat the delicate internal parts of the machine, affecting its performance.

Samples must be smaller than 2.5 cm in diameter so as to fit within the target specimen holders utilized by the microprobe. All samples have to be polished to a mirror finish because an uneven sample surface can deflect electrons and emit x-rays in undesirable directions. Preparation to flatness without altering sample composition is difficult, especially with porous materials such as bone, because polishing compounds can become lodged inside pores, but since the microprobe is capable of viewing the sampling area in great detail, inclusions can be recognized and

compensated for or they can be circumvented in the course of analysis.

As stated above, microprobe analysis was preceded by total compositional analysis in order to make optimum use of the microprobe analysis. This optimum use also included the amount of time that the machine was to be utilized because demands for use of the microprobe were great at the time of my experiments. Since it is the concentration of an element that is discerned in microprobe analysis, the identification of an element in certain quantities at one point may differ vastly from concentrations of the whole sample. What may be a major element in a small area of concentration may be a trace element in the whole sample. Therefore, electron beam scanning techniques can provide useful information on the distribution of elements over an area and are useful for examining morphological features. In bone, for example, compositional changes or growth history can be examined by analyzing the distribution of elements over an area and within specific morphological features.

Because discrete points can be located and examined, microprobe analysis can be useful for discerning variations in composition of mineral phases in regards to zonal relationships and for the determination of the association of minor elements within major ones. These types of data could be especially useful in bone analysis because any one bone can contain up to five mineral phases of hydroxyapatite at any one time and substitutions can occur at various

stages of bone growth. If specific zones or growth areas of bone can be isolated and identified on the basis of the constituent elements, seasonality factors and post-depositional changes may be documented.

In microprobe analysis traverses can be made in several directions so that zonal relationships can be identified and the question of homogeneity versus variability or heterogeneity can be explained. This illustrates the ability of the microprobe to determine the extent of concentric zoning which should be exhibited by bone lamellation.

In the microanalysis in this study I attempted to determine:

1. ratio differences between elements
2. differences in composition of each bone
3. patterned variability in morphological features such as cortical and trabecular bone
4. elemental differences between external cortical bone and internal cortical bone (where applicable)

These data would be informative if the rate of exchange of elements during bone growth and development could be identified and the removal of elements by post mortem or post-depositional factors could be ascertained. Thus, if the leaching of elements over time due to the disintegration of bone could be ascertained, placement of individual bones in a chronological sequence could be done based on the relative occurrence of constituent elements.

V. Results: Part I

The results of the ICP analysis are presented in Table 3. These results were compared with data from biological and medical studies to evaluate the precision of the present technique. This was done with the knowledge that comparisons of these two types of data, from different species, is only qualitative at best (Rowland et al., 1959), and that substantial variations in analytical values have been reported in interlaboratory and intermethod comparison exercises (Bowen, 1975). But lacking a Standard Reference Material for bone, some verification of the analytical method was thought necessary. In keeping with the convention adopted by the International Commission on Radiological Protection, median values are used for purposes of comparison of results to prevent skewness caused by any 'wild' concentrations (O'Connor, 1980).

The median values for calcium and phosphorus were 23.3 per cent and 11.1 per cent, respectively, which correlate well with figures accepted for mammalian bone (Vinogradov, 1953; Underwood, 1977). The amounts of many other elements (Cd, Cu, Fe, K, Mo, Na, Ni, Zn) approximated expected values so the analytical results appear to correlate well with other bone analyses (Skinner et al., 1972; Gawlik, 1981; Kirchgessner and Neese, 1976) (Table 3).

Comparing the figures for condyles only, some intra-species differences were observed on age and sex variables. Excluding the values for the young juvenile

Table 3: Results of ICP Analysis I

Specimen	Ag	Al	B	Ba	Be	Ca	Cd	Co
Adult Female								
rt. condyle	4.6	35.3	13.6	98.6	<1	16.2	<2	<2
rib	6.1	83.1	7.8	103.6	<1	22.5	<2	2.1
femur	0.6	27.3	19.0	161.7	<1	40.6	2.2	4.9
premaxilla	9.2	66.3	5.3	110.3	<1	20.6	<2	<2
mandible	7.2	46.6	7.4	94.6	<1	26.2	<2	<2
Adult Male								
rt. condyle	9.7	15.8	9.5	90.9	<1	24.8	<2	<2
femur	9.7	12.3	10.1	123.0	<1	35.0	<2	3.0
rib	7.5	27.3	6.1	89.9	<1	25.1	<2	<2
mandible	7.7	20.0	5.9	76.8	<1	28.5	<2	2.3
innominate	6.9	41.0	3.6	71.2	<1	25.5	<2	2.0
Subad. Male								
rt. condyle	8.6	27.6	9.5	86.2	<1	23.3	<2	2.3
Subad. Female								
rt. condyle	5.3	29.8	6.7	69.4	<1	21.8	<1	<2
Indet. Immat.								
rt. condyle	8.2	163.0	4.6	185.0	<1	24.4	<2	<2

Note: All element values indicate parts per million
except Ca and P which are in percentages

cont. Table 3:

Specimen	Cu	Fe	K	Li	Mg	Mn	Mo	Na
Adult Female								
rt. condyle	2.2	80.3	863	34.6	2480	2.0	3.5	3900
rib	1.9	73.2	455	53.7	3050	3.1	2.9	4455
femur	1.9	19.5	589	58.5	5733	2.2	3.0	7638
premaxilla	2.5	89.2	1421	57.9	3025	2.6	3.9	5780
mandible	1.3	41.5	485	38.9	2999	1.7	1.9	4400
Adult Male								
rt. condyle	2.0	40.2	757	59.9	3470	2.4	2.8	4980
femur	1.4	23.6	755	58.4	4060	6.1	1.9	5500
rib	1.9	10.0	1705	61.5	3345	3.7	3.5	5087
mandible	1.1	38.2	1064	40.6	3312	2.8	1.9	4775
innominate	1.3	74.7	921	44.0	3007	4.2	1.6	3939
Subad. Male								
rt. condyle	1.9	99.7	203	60.4	3955	2.3	2.5	3668
Subad. Female								
rt. condyle	1.1	65.1	779	33.0	2724	1.2	1.8	3745
Indet. Immat.								
rt. condyle	2.5	362.0	2585	67.2	4180	14.6	3.9	8473

Note: All element values indicate parts per million
except Ca and P which are in percentages

cont: Table 3

Specimen	Ni	P	Pb	Si	Sr	Te	Ti	V	Zn
Adult Female									
rt. condyle	3.5	7.6	19.8	17.8	62.6	28.5	<2	3.5	93.0
rib	3.4	10.4	78.8	38.8	78.7	36.2	<2	4.8	78.6
femur	4.5	19.9	28.9	39.2	138.0	72.6	<2	7.5	146.5
premaxilla	3.9	9.8	10.7	35.3	80.9	48.6	<2	5.0	67.9
mandible	2.4	12.4	15.8	16.3	70.6	43.2	<2	4.1	68.0
Adult Male									
rt. condyle	2.8	11.7	32.0	38.7	58.7	34.9	<2	5.1	78.0
femur	1.9	16.6	26.1	17.9	86.6	55.7	<2	5.5	96.4
rib	3.5	11.9	26.3	34.9	66.0	48.2	<2	4.5	80.5
mandible	2.3	13.5	16.8	13.3	53.9	42.8	<2	4.3	68.2
innominate	2.2	12.0	17.8	12.5	49.3	36.6	<2	4.1	72.0
Subad. Male									
rt. condyle	2.5	11.1	25.3	18.9	70.9	41.5	<2	5.2	100.0
Subad. Female									
rt. condyle	1.8	10.3	13.2	10.9	52.4	32.3	<2	3.2	58.3
Indet. Immat.									
rt. condyle	3.9	11.7	16.4	17.2	106.0	46.5	<5	5.6	129.0

Note: All element values indicate parts per million ,
except Ca and P which are in percentages

animal, females had marginally higher values than males for Al (33%) and K (43%). Males had marginally higher values for Ag (50%), Ca (15%), Li (44%), Mg (30%), P (20%), Pb (43%), Si (50%), Te (20%), and V (30%). Subadults of both sexes were highest in iron but had lower values for most of the other elements. The young juvenile animal exhibited the greatest deviations from the median values and had the highest values for most elements. High values are not uncommon in foetal or very young juvenile animals as the degree of vascular recruitment is high due to very active bone growth (Kirchgessner and Neese, 1976; Casey and Robinson, 1979).

On the basis of the median values for the adult male and adult female samples, the female was higher in Al (57%), Ba (14%), Fe (48%), Si (50%), and Sr (25%). The male was higher in K (38%) and Pb (30%).

The above results warrant further investigation for they may indicate definite patterned relationships. But, since ICP analysis was initiated to establish the range of elements and the quantities of elements so that microprobe analysis could proceed more efficiently, the causes of these differences were not investigated.

For the internal microprobe analysis, eight right condyles were selected for examination. These consisted of seven archaeological specimens and one modern specimen (Table 4). Since the samples had to conform to the size restrictions imposed by the microprobe, representative

Table 4: Bone Samples Used For Electron Microprobe Analysis

Animal No.	Sex	Age
61	Female	5
144	Male	4
251	Male	5
278	Female	3
280	Male	8
363	Male	7
372	Male	4
382	Subadult Male	2

pieces were cut from the central portion of the condyles. The sample population consisted of 5 adult males, 1 adult female, 1 subadult male and 1 subadult female. The subadult male was the only modern specimen prepared.

For the first exploratory analysis, transects were run across sample 144 starting at the extreme outer edge of the cortical area toward the center. The first transect consisted of point by point analysis using a beam of focus of one square micron. Immediately there were problems of burning at the sampling site and bubbles began to form. These bubbles were caused by the fatty substances still contained within the old bone. The high combustibility of the organics within the bone could be compensated for by either reducing the initial energy of the beam of electrons striking the sample, or by rastering the beam over a larger area. Both of these solutions had drawbacks. Reducing the initial energy of the beam would reduce the incidence of x-ray or photon emission and would thus lower detectability for most elements and particularly for the minor elements. Rastering over a larger area would eliminate all the proposed experiments involving discrete points of analysis.

Since reducing the initial energy of the electrons was so restrictive, affecting the whole range of elements, and thereby all the experiments, rastering was the only alternative because some analyses could still proceed. After a few attempts, 90 x 90 microns was selected as the optimum size of the rastering area.

Once the problem of volatilization was solved, compositional analyses began. The results were not immediately encouraging. High background interference obscured all the minor and trace element emission peaks and only calcium and phosphorus peaks were discernible. In fact, it was the high calcium and phosphorus levels that obscured the other element peaks.

This problem arose because of the inherent nature of microprobe analysis, in that it employs a counter which detects the number of emitted x-rays or photons. Since the microprobe was being rastered over an area of 8100 square microns and penetrating to a depth of one micron, the massive amounts of parent material (in this case the calcium phosphate based hydroxyapatite) caused the detection limits of the other elements to increase to unreadable levels. The reason for this is that if only a few atoms of an element are present within the microvolume being excited, the chances are extremely small that these atoms will be excited enough to emit an x-ray or photon and smaller still that the emission will be in the direction of the detector.

Since calcium and phosphorus were the only elements detectable using this technique, it was hoped that spatial distribution or ratio differences between these two elements could be detected.

A gradual increase in both calcium and phosphorus levels was detected moving from the exterior of the cortex towards the interior (Table 5), but the increase was not

Table 5: Results of Electron Microprobe Analysis

Sample	Location	Total Counts		Ratio
		P	C	P/Ca
144	Trabecular	274008	369179	0.7422
382	Trabecular	276044	375416	0.7353
144	Cortical	277185	379479	0.7304
382	Cortical	267997	374683	0.7153
278	Trabecular	272184	382428	0.7177
372	Trabecular	272581	384487	0.7089
278	Cortical	264098	385007	0.6860
372	Cortical	245555	354766	0.6922

sufficiently different to be quantifiable except on a counts per second basis. There were also slight variations in these levels within the microstructures of the cortical and trabecular areas, but these too were not quantifiable. No detectable variation in the calcium/phosphorus ratio appeared at any time during the investigations of different bone nor in different areas of the same bone. It seemed unlikely that ratio differences would be apparent when the beam of focus covered such a large area. No quantifiable differences were apparent between the old bone samples and the bone from the modern specimen. The only major difference was that the modern material did take less time to begin burning, due to the presence of more volatile organics.

The volatility of the organic matrix plus the high calcium and phosphorus content within bone precluded a satisfactory conclusion to the experiments. Since exact elemental composition at discrete points of one square micron were the focal point of these experiments, forced rastering of the electron beam over larger areas effectively eliminated the analytical advantages that prompted the use of the electron microprobe for analysis of these archaeological bone materials.

VI. Analysis: Part II

The inherent deficiencies of the microprobe analysis of bone prompted a re-examination of ICP analysis since the preliminary ICP results appeared encouraging. An extension of my Boreal Institute grant enabled me to complete a more detailed examination of the use of the ICP for bone analysis.

The ICP results in Table 3 revealed differences in the elemental make-up of bones depending on the age and sex of the animal sampled. Also, differences were noted between various bones from the same animal. It should be noted here that differences in quantities or ratios of elements can be expected between animals because of differential soil intake (Healy, 1974). Grazing animals ingest soil along with their herbage and this can be a major source of elemental intake. Healy reports that annual ingestion of soil can reach 75 kilograms for domestic sheep and up to 600 kilograms for dairy animals, with individual animals in a flock or herd differing by a factor of two or more. Since intake of soil elements directly affects uptake of elements within bone, variation between animals even of the same sex and age group can be expected.

For the second stage of analysis it was decided to select bones from within one rigidly defined group so as to keep the number of interfering variables to a minimum. Criteria for selection were as follows: 1) all condyles selected were to be pointing straight upwards so as to

preclude ground-water or soil contamination; 2) all condyles had to be from animals of the same sex and age group; 3) there had to be representation of animals from throughout the site to test for spatial differences.

Following these criteria, pairs of condyles from 17 adult females were selected for analysis from the sample population. These animals came from four areas of site PjRa-18 (Fig. 7). Right condyles were used in the first series of analyses following the wet-ashing procedures employed in the first ICP analysis described above. Left condyles were used in a second series of analyses employing a dry-ashing technique described below.

Both procedures have been used in other studies with varying degrees of success (Hyvönen-Dabeck, 1981; Scott and Stasheim, 1975; Koirttyohann and Hopkins, 1976; Friend et al., 1977; Cheng and Agnew, 1974; Anderson, 1972; Giron, 1973; Keeley et al., 1977; and Locke, 1980; Moo and Pillay, 1983; and Hall et al., 1984). I decided to run parallel tests in order to determine the effect of these ashing procedures on the analytical precision of ICP analysis of bone material. Also, the inclusion of both techniques would help to facilitate interstudy comparisons since various studies have expressed results in terms of either whole bone dry weight (for wet-ashing) or ashed weight (for dry-ashing).

For the dry-ashing procedure the samples were oven dried at 105 degrees Celcius for 24 hours, whereupon the

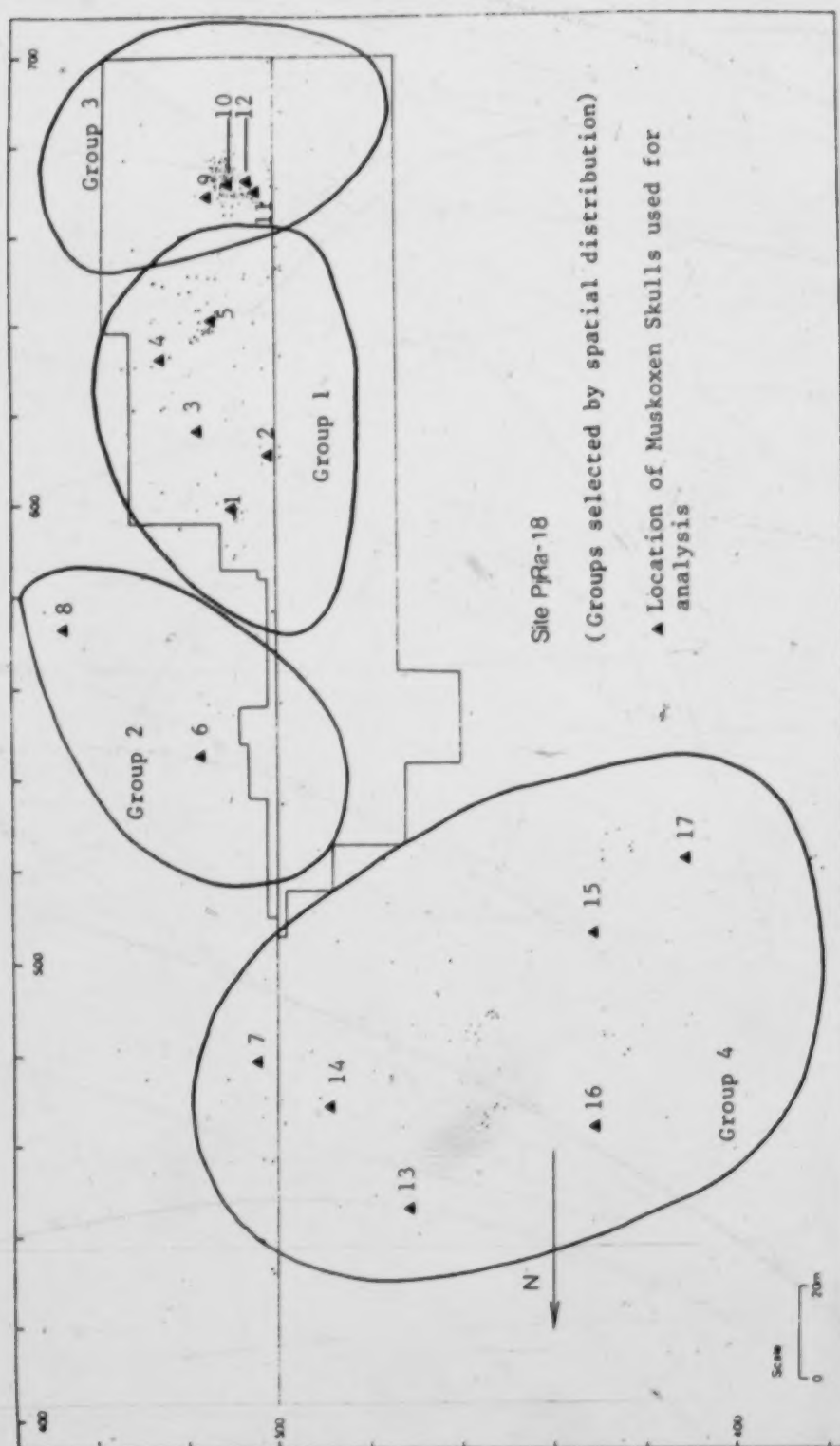


Figure 7: Location of Muskoxen Skulls utilized for analysis

weights were recorded. This procedure was to eliminate most of the water loosely bound within the samples. The samples were then ashed in a muffle furnace at 550 degrees Celcius for 24 hours, then weighed again after equilibration to room conditions. The ashed samples were digested with nitric and perchloric acids, then diluted to 100 millilitres using distilled water.

Due to the absence of a bone standard to aid in calibrating the results for interstudy comparisons, an artificial reference solution was created using reagent grade calcium and phosphorus. First an ICP analysis for calcium and phosphorus was undertaken for all 17 bone samples, then the median values for these were used to create the standard compound. Standards and blank samples were introduced after every third unknown as this is a good means of monitoring instrument stability and quality of the analysis. Analyzing referrent samples with known concentrations provides an estimate of the combined accuracy and precision of a semi-quantitative procedure (Brenner et al., 1984; Zhuang and Barnes, 1984).

VII. Results: Part II

The results of the second set of ICP analyses are presented in Table 6 and 7. Table 6 lists the analysis results of the samples that were wet ashed. The elements listed here are those that were selected for in advance on the basis of the previous analysis results (Table 3). To keep costs of analysis down only those elements that had readings greater than 20 parts per million were selected. This number was chosen because if differences in values were significant, elements with low parts per million levels could drop below their detection limits.

The results from the two wet-ashed procedures (Tables 3 and 6) were examined to test the original hypothesis that there should be a detectable decrease in the amounts of elements from the older bone material in comparison to the modern material. No observable pattern was evident. For the old material six elements had lower readings (Ca, K, Li, Na, Pb, and Te), seven showed increases (Al, Ba, Fe, Mg, Si, Sr, and Zn), while phosphorus remained the same. For the minor elements it is interesting to note that lithium all but disappeared while Mg, Na, Te, and Zn were only marginally different.

Table 7 presents the results of the dry-ashed sample analysis. Here, no particular elements were requested, so the full capability of this ICP machine (26 elements) was used. Also, for purposes of comparison four modern bone samples were analyzed along with the 17 archaeological

Table 6: ICP Results II (Wet-Ashed)

Specimen	Al	Ba	Ca	Fe	K	Li	Mg
1	29.0	178	20.8	55.2	265	2.4	4040
2	122.0	175	18.3	246.0	454	2.3	3760
3	64.4	175	16.2	112.0	472	1.4	4140
4	69.7	194	18.3	140.0	387	1.8	3890
5	75.6	240	20.1	128.0	407	2.0	4000
6	367.0	177	17.7	518.0	762	1.9	4040
7	245.0	229	23.9	428.0	474	2.0	3800
8	119.0	161	17.2	157.0	441	1.0	3560
9	283.0	148	17.8	317.0	594	1.7	3360
10	56.5	179	16.6	121.0	478	0.9	3340
11	125.0	186	21.3	276.0	573	1.3	4300
12	73.4	184	17.5	88.1	395	1.7	3600
13	116.0	235	20.4	152.0	439	2.2	3940
14	200.0	236	21.1	256.0	394	2.1	4360
15	336.0	188	15.5	367.0	520	1.4	3680
16	99.4	242	20.6	175.0	403	2.2	3520
17	147.0	151	17.2	172.0	415	1.4	3610

Note: all element values indicate parts per million
except Ca and P which indicate percentages

cont. Table 6:

Specimen	Na	P	Pb	Si	Sr	Te	Zn
1	4141	11.4	10.90	51.1	108.0	20.7	129.0
2	3020	10.30	9.51	77.2	88.6	19.4	77.8
3	3670	9.37	9.30	56.6	54.3	18.6	104.0
4	3200	10.50	10.40	57.8	69.4	20.3	104.0
5	3400	10.50	11.50	62.9	86.8	21.2	121.0
6	2420	9.35	9.70	98.5	111.0	19.2	112.0
7	3050	10.90	13.10	66.3	95.7	22.7	113.0
8	2660	10.20	9.54	57.9	57.8	19.4	111.0
9	2690	9.70	9.83	77.9	55.4	19.3	92.8
10	2580	9.30	9.12	51.3	48.5	18.1	90.0
11	3095	9.85	12.50	51.8	81.9	21.6	93.9
12	2860	9.77	9.17	44.1	55.7	18.4	84.7
13	3430	11.30	12.40	61.5	110.0	22.9	113.0
14	2920	10.90	12.30	70.9	104.0	22.5	108.0
15	2630	9.42	9.72	101.0	86.0	19.6	96.6
16	3310	10.60	12.30	46.0	105.0	22.4	100.0
17	2730	9.85	10.50	55.3	76.7	20.3	110.0

Note: all element values indicate parts per million
except Ca and P which indicate percentages

Table 7: ICP Results III (Dry-Ashed)

Specimen	Al	Ba	Ca	Cu	Fe	K	Mg
1	133	289	37.2	<5	129	825	5950
2	902	322	36.5	<5	1020	739	5750
3	563	309	36.4	<5	568	791	6520
4	444	340	35.5	<5	508	782	5710
5	277	393	33.8	<5	285	585	5650
6	663	351	34.9	<5	781	1000	6260
7	731	418	35.2	<5	885	864	6260
8	404	294	36.1	<5	459	886	5990
9	583	361	35.4	<5	420	657	5880
10	534	334	36.6	<5	454	681	6360
11	342	340	35.9	<5	387	721	6990
12	356	355	36.3	<5	429	647	5640
13	434	395	35.2	14	433	540	5720
14	288	416	35.3	<5	312	331	6760
15	1120	346	35.9	23	1040	945	6230
16	443	453	36.9	<5	571	549	6090
17	521	287	35.6	<5	415	607	6610
18 (modern)	367	260	36.4	<5	324	522	6630
19 (modern)	283	226	35.1	<5	265	719	6480
20 (modern)	311	303	36.3	<5	217	897	6090
21 (modern)	91	190	36.5	<5	194	430	7040

Note: all element values indicate parts per million
except Ca and P which indicate percentages

cont. Table 7:

Specimen	Mn	Na	P	Pb	Si	Zn
1	<5	5670	17.9	<5	913	208
2	16	4640	18.1	<5	9600	168
3	9	5160	17.8	<5	5560	187
4	9	4640	17.3	<5	4790	172
5	9	4940	16.6	<5	1550	190
6	12	4180	17.1	<5	7340	206 ^p
7	<5	4630	16.9	<5	6580	207
8	<5	4480	17.6	<5	2940	210
9	8	5290	17.0	<5	4450	169
10	<5	4721	17.9	<5	3650	180
11	<5	4810	17.3	<5	3039	171
12	<5	4340	17.7	<5	4860	181
13	<5	4420	17.3	<5	3240	194
14	8	3680	17.4	<5	2570	190
15	17	3980	17.2	8	9220	166
16	<5	4830	17.6	<5	1970	206
17	<5	4820	17.3	<5	3940	205
18 (modern)	30	5200	18.0	<5	1903	153
19 (modern)	<5	7990	17.4	<5	1200	164
20 (modern)	<5	7590	17.7	<5	870	224
21 (modern)	<5	6420	18.2	<5	1120	201

Note: all element values indicate parts per million
except Ca and P which indicate percentages

specimens. The 13 elements in Table 7 represent those that registered above the detection limits of the machine.

In comparing the results of the wet and dry procedures it was found that most element levels increased by a factor of two, except aluminum (factor of 3) and silicon (factor of 70) (Table 8). This doubling of values was predictable because the weight loss of organic matrix upon ashing is 40 to 60 per cent (Table 9). The calcium/phosphorus ratio for the dry ashing was 2:1, for wet ashing it was 1.86:1, while the theoretical ratio for bone hydroxyapatite is from 1.0 to 1.66:1 (molar) (Neuman, 1980), or 1.2 to 2.15:1 (weight) (Skinner, 1972). The calcium and phosphorus values appear remarkably constant in all samples and appear unaffected by the age of the materials.

Among the dry-ashed samples, comparing the 17 old samples to the four modern ones, no discernible pattern was evident. Five elements showed increases (Al, Ba, Fe, K and Si), one showed a decrease (Na), while seven remained the same or showed only marginal differences (Ca, Cu, Mg, Mn, P, Pb and Zn). Most of the elements of the old bone material showed increases or decreases relative to the new bone material by about the same factor as in the wet analysis.

It should be noted that lead levels dropped to just above detection limits after the dry-ashing procedure while strontium and tellurium levels dropped below detection limits. Very low readings were obtained for copper and manganese as in the initial study (Table 3), but lithium

Table 8: Comparison of Means

Element	Wet-Ashing	Dry-Ashing	Factor of Increase
Al	148.7	509.7	≈ 3
Ba	195.7	345.7	≈ 2
Ca	18.9	35.8	≈ 2
Cu		<5.0	
Fe	218.0	536.7	≈ 2
K	464.2	757.8	≈ 2
Li	1.78		
Mg	3761.0	6134.2	≈ 2
Mn		7.83	
Na	3047.4	4623.3	≈ 2
P	10.17	17.38	≈ 2
Pb	11.27	<5.0	
Si	64.0	4552.2	≈ 70
Sr	82.0	—	
Te	20.3		
Zn	102.2	190.5	≈ 2

Table 9: Ash Content of Dry-Ashed Bone

Specimen No.	Ash(% by weight)
1	64.4
2	62.8
3	60.3
4	60.1
5	62.4
6	57.8
7	60.8
8	59.8
9	56.1
10	57.7
11	58.9
12	60.5
13	65.1
14	63.0
15	56.7
16	60.8
17	57.8
18	49.6
19	43.7
20	44.0
21	57.5

values were below detection limits, even in the modern samples. The high temperature used in the dry-ashing procedure could have caused the volatilization of lithium, lead, strontium and tellurium, yet the ashing temperature was comparable to those used by other researchers (Langmyhr and Kjuus, 1978; Hyvönen-Dabek, 1981; Scott and Strasheim, 1975; Koirttyohann and Hopkins, 1976; and Anderson, 1972), whose ashing temperatures ranged from 450 to 1000 degrees Celcius. Only Anderson reports losses of lead at temperatures between 450 and 500 degrees Celcius. The loss of these elements could have been the product of high temperature or could have resulted from these elements adhering to the surface of the crucibles used in the muffle furnace.

Since no discernible pattern emerged from a visual examination of the data, these data were assessed statistically. Procedures for these analyses were derived from the Michigan Interactive Data Analysis System computer program (MIDAS). For this study separate tests were run on the two sets of data. The wet ashed set consisted of all 17 samples from Table 6 and the single female adult condyle listed in Table 3. The second set consisted of the 17 old samples and the single modern female adult from Table 7 (no. 18).

In all cases, calcium and phosphorus were excluded from the statistical analyses because the measurements were not comparable (per cent versus parts per million) and the

conversion to parts per million would have resulted in values that would drastically skew the results.

For the purpose of the tests, the old material was divided into four discrete groups based on their areal distribution on site PjRa-18 (Fig. 7). The areas are representative of the postulated developmental sequence at the site: the southern area is thought to represent the earliest occupation while the northern area represents the most recent occupation (Hickey, personal communication, 1981). Group 3 comes from the southernmost area while group 4 comes from the northernmost. On the basis of the physical appearance the bone material from group 3 shows more gross deterioration than does the material from group 4. Group 1 is contiguous with group 3 but superposition of bone material over tent ring remnants indicate at least two separate occupations within this area. Therefore, group 1 could represent a separate occupation from groups 3 and 4 or it could be the processing-disposal area for the group 4 occupation. Group 2 lies between groups 1 and 4 and could represent surface scatter from any group. Group 5 consists of the modern control specimens. For the purpose of these statistical analyses, each group is assumed to be a random sample from a discrete area of the site.

Descriptive statistics were run on the data and the results are listed in Table 10 (wet-ashed) and Table 11 (dry-ashed). From Table 10 two separate test sets were derived. The first set includes all 12 elements while for

Table 10: Group Means For Wet-Ashed Bone

Element	Group 1	Group 2	Group 3	Group 4	Group 5
Al	72.14	243.67	134.48	179.68	35.30
Ba	192.40	189.00	174.25	210.40	98.60
Ca	18.74	19.6	18.3	18.96	16.20
Fe	136.24	367.67	200.53	224.40	80.30
K	397.0	559.0	510.0	434.2	863.0
Li	2.0	1.69	1.46	1.88	34.6
Mg	3966	3800	3650	3822	2480
Na	3486.2	2710.0	2806.3	3004.0	3900.0
P	10.4	10.15	9.65	10.4	7.63
Pb	10.32	10.78	10.16	11.44	19.8
Si	61.12	74.23	56.28	66.94	17.8
Sr	81.42	88.17	60.38	96.34	62.6
Te	20.04	20.43	19.35	21.54	28.5
Zn	107.16	112.0	90.35	105.52	93.0

Note: Group 5 consists of one modern specimen

Table 11: Group Means For Dry-Ashed Bone

Element	Group 1	Group 2	Group 3	Group 4	Group 5
Al	463.8	533.5	453.75	589.5	367.0
Ba	330.6	322.5	347.5	385.83	260.0
Ca	35.88	35.5	36.05	35.85	36.4
Cu	<5.0	<5.0	<5.0	9.5	<5.0
Fe	502.0	620.0	422.5	609.33	324.0
K	744.4	943.0	676.5	639.33	522.0
Mg	5916.0	6123.0	6217.5	6278.3	6630.0
Mn	9.6	8.5	5.75	7.5	30.0
Na	5010.0	4330.0	4790.3	4393.3	5200.0
P	17.5	17.35	17.47	17.2	18.0
Pb	<5.0	5.5	<5.0	5.5	<5.0
Si	4482.6	5140.0	3999.8	4586.7	1903.0
Zn	185.0	208.0	175.25	194.67	153.0

Note: Group 5 consists of one modern specimen

the second set sodium and magnesium were excluded because their high values could obscure differences existing between elements with low numerical values. Likewise, the material from Table 11 was divided. The first set includes all the elements while the second set excludes copper, lead and manganese because the unquantified values obtained for these elements were not deemed sufficient for these analyses. For the purposes of all the tests run in this study, probability levels of 0.05 or less were considered to be statistically significant.

To test the possibility of inter-group differences, statistical evaluation of the numerical data was undertaken. The statistical tests carried out were the t-test, the pairwise rank test, parametric correlations (using Pearson's R), non-parametric rank correlations, and univariate one-way analysis of variance tests. The null hypothesis being tested in all cases is that there is no difference between the means. The results of these tests are listed in Tables 16 through 29 (Appendix 1).

Though the data indicates that there is considerable overlap and variation in a number of measurements and that no one group emerges as being significantly different from the others, a closer examination of the data results reveals some interesting tendencies (Tables 12 and 13). In the pair-wise tests whenever differences arise, group 3 is involved and in the group correlations, the modern specimen is involved. Although the evidence is meagre, group 3 does

Table 12: Summary of Tables 16 thru 22 (Wet-Ashed)

Table 16

-no significant differences between the means

Table 17

-differences at the .05 level between Groups 2
and 3

Table 18

Twelve Elements

-differences at the .01 level between Groups 2
and 3

-differences at the .01 level between Groups 3
and 4

Ten Elements

-differences at the .01 level between Groups 2
and 3

-differences at the .05 level between Groups 3
and 4

Table 19

-all groups show high correlations

Table 20

-all groups show high correlations

Table 21

-all groups show high correlations

Table 22

-differences at the .01 level between Groups 2
and 5; 3 and 5; and 4 and 5

Table 13: Summary of Tables 23 thru 29 (Dry-Ashed)

Table 23

-differences at the .05 level between Group 1
and 3, 2 and 3, and 3 and 4

Table 24

-no significant differences between the means

Table 25

Eleven Elements

-differences at the .01 level between Groups 1
and 3, and groups 3 and 4

-differences at the .05 level between Groups 2
and 3, and groups 4 and 5

Eight Elements

-no significant differences between the means

Table 26

-all groups show high correlations

Table 27

-group 5 is different at the .01 level from all
other groups

Table 28

-group 5 is different at the .01 level from all
other groups

Table 29

-differences at the .01 level between Groups 2
and 5, and Groups 4 and 5

emerge as having some statistically significant differences from the other groups. The fact that the 2 modern female samples show differences in correlation is less significant since these single individuals with their inherent individual variation are the sole representatives of their experimentally discrete populations.

To determine whether or not differences exist between the group means, univariate one-way analysis of variance tests were undertaken. In this equality of variance test the variances are assumed to be the same. Tests were first run on the raw data then the raw data were transformed into natural logs to equalize group variances. The null hypothesis being tested here is that the means are not different.

The results of these analyses are presented in a simplified form in Tables 14 and 15.

For the wet-ashed material zinc shows the most consistent variability with differences at the 0.01 significance level between groups 2 and 3 and groups 3 and 4. Analysis was not possible between groups 1 and 2 and groups 1 and 3 because the group variances were not equal. But, differences in variances also indicate differences between the groups. For the dry-ashed material the same groups show variances at the 0.01 level for zinc (groups 2 and 3; and groups 3 and 4). Group differences were also apparent between Groups 1 and 3 for Ba, Fe, Mn and Si.

Table 14: Summary of Analysis of Variance (Wet-Ashed Bone)

Significant at the .05 level

	Groups					
	1/2	1/3	1/4	2/3	2/4	3/4
Al	.0211		.0208			
Ba						
Fe	.0573					
K						
Li						
Mg						
Na	.0298	.0204				
Pb						
P						
Si						
Sr						.0069
Te						.0676
Zn	X			.0006	X	.0057

X = variances are not equal

Table 15: Summary of Analysis of Variance (Dry-Ashed Bone)
Significant at the .05 level

	Groups					
	1 and 2	1 and 3	1 and 4	2 and 3	2 and 4	3 and 4
Al						
Ba		X				X
Cu						
Fe		X		X		X
K	.0735		X	.0031		X
Mg						
Mn		.0843				
Na	.0794		.0543			
Pb						
Si		X				
Zn				.0031		.0529

X = variances are not equal

The results of the statistical manipulation of the data are generally inconclusive. The means are shown to be consistently similar even though the individual values show considerable variation about the means. In fact, the numerical data show considerable overlap. But, when differences arose in the statistical assessment of the numerical data, group 3 was usually involved.

Though individual element readings for the two ashing procedures are not consistent, group 3 appears to have the lowest element values overall. Groups 2 and 4 appear to be the most similar having consistently higher rankings than the other two groups. Group 1 ranks between groups 2 and 4 and group 3. On the basis of the statistical analyses group 3 does appear to be different from the other groups.

VIII. Discussion and Conclusions

On the basis of the present analytical results, I would have to conclude that my original hypothesis was correct; bone mineral elements are leached out of bone over time in sufficient quantities so as to enable the determination of chronologically discrete sub-units of large arctic multi-component surface sites.

In this study the assumption underlying all the experiments was that the age of a particular bone is reflected in the presence or absence of elements within the bone. But, it was stated that since the conditions for bone preservation were good, elemental differences between bones from within a narrow time period were expected to be slight.

Thus it is encouraging that the statistical manipulation of the data proved to be so successful. On the basis of statistical evaluation of the data, it appears that all the material came from the same statistical population, but some internal differences were shown to exist. Perusal of the raw data from Tables 6 and 7 shows that slight areal differences are indicated. Since the differences were expected to be slight, the tenuous nature of the results of these experiments is not surprising.

The experimental results are encouraging because even if the expected overall pattern of loss was not identified, some tendencies were shown to exist. And, these tendencies match the suspected developmental sequence postulated for site PjRa-18 on the basis of standard archaeological

assessment.

Hickey proposed that there were at least two discrete occupations at site PjRa-18 based on superposition of artifacts and artifact clustering. He speculated that the southernmost area was occupied earliest with at least one subsequent occupation utilizing the remainder of the site. On the basis of the present analytical results, the southernmost area does appear to contain bones that have been modified chemically in sufficient amounts to indicate a separate occupation. Bones from the other areas appear to be so chemically similar that no conclusions can be reached as to their chronological stratification.

Further study using a larger sample size could provide results that are statistically more significant. Also a larger sample size would reduce errors due to inter-animal variability and the possible inclusions of animals from without the specific chronological population. A larger sample size would also enable the isolation of specific elements as being the demarcators of patterned elemental loss since inter-animal variability would be reduced as a factor.

This study examined two different techniques for the ashing of bone material and has found the results to be very similar. Therefore, neither method is being endorsed or rejected as the method of choice. One recommendation for the dry-ashing technique is that low temperature ashing be used (below 400 degrees Celcius) to prevent volatilization of

some elements. This could make the results of the two techniques even more similar if the same elements could be detected and compared. But, no matter which technique is used, it does seem imperative that a bone standard be used so that interstudy comparisons can be affected. At present no two studies have been located which present their results with reference to a bone standard with sufficient clarity so as to make interstudy comparisons valid.

The present study was only a preliminary work with neither formalized procedures and few established reference data. As such the study tested analytical techniques in an attempt to derive specific information regarding bone analysis that could be of benefit for the interpretation of Arctic archaeological site developmental sequences.

While adding to basic knowledge and extending analytical techniques, this study demonstrates that the general biophysical design of bone with its complex organic matrix does not lend itself to examination by the electron microprobe. While some information was gathered using this technique, it was of a qualitative nature only and most of the hoped for results were not realized. The ICP results on the other hand show great promise and this technique may be applied to a wider range of archaeological problems.

I feel that total compositional analysis using ICP can be of great utility in faunal analysis. Just as compositional analysis has been used to address problems of ceramic, metal and obsidian origins, so too can it be used

to assess the origins of faunal materials. This is not an unreasonable expectation since the bioavailability of elements is determined by environmental factors. Wessen et al. (1978) have noted that barium content differences can be used to distinguish marine bone from terrestrial bone. Terrestrial bone identification on the basis of geographical location could also be accomplished by total compositional analysis due to the fact that each micro-environment is unique. Pedogenesis and physiographic region have the most influence on bioavailability of elements, and variability is thus assured. A number of factors which cause differences in the availability of elements to plants and thus ultimately to the animals which eat them are:

1. microbiological activity
2. soil drainage and oxidation-reduction conditions
3. weather conditions and seasonal variation
4. parent material sources
5. organic matter content of the soil
6. soil texture and make-up

These conditions vary greatly between areas, and thus variability is assured.

Even though animals maintain roughly the same proportions of the essential elements in their bodies, biogeochemical factors will act to introduce different proportions of elements into the body which will be absorbed and stored within the tissues and skeleton.

Given that the environment dictates the number of potential elements available, the skeleton of an animal acts as a reservoir for these elements. Analyzing for major, minor and trace elements could allow for the identification of peculiar patterns of elemental combinations relying on up to 60 different elements, and would permit the 'fingerprinting' of bones on the basis of their constituent differences.

Applications of this type of information could be useful for examining questions concerning prehistoric technology, economy or social organization. For example, processed bone artifacts of unknown geographical origin could be analyzed to determine source areas of the raw bone material, thereby offering hope of determining trade networks or seasonal round.

This is but one of the possible applications for total compositional analysis of bone, but the focus of this study was not the application of this type of analysis as it has been in checking the feasibility and accuracy of analysis of bone material. I am convinced that radio frequency inductively coupled argon plasma atomic emission spectrometry is probably the most convenient and accurate method for this type of analysis and think that further experiments with this machine are warranted.

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IX. APPENDIX 1

Table 16: Results of T-test (Wet-Ashed Bone)

Twelve Elements				
Group	Mean	Std Dev	T-Stat	Signif
1	711.00	257.43	.39853	.6979
2	681.39			
1	711.00	219.13	1.0783	.3040
3	642.79			
1	711.00	154.96	.65891	.5235
4	681.53			
1	711.00	482.20	.49003	.6337
5	642.79			
2	681.39	72.57	1.8424	.0925
3	642.79			
2	681.39	107.76	-.4554	.9964
4	681.53			
2	681.39	553.72	.2414	.8136
5	642.79			
3	642.79	75.07	-1.7875	.1014
4	681.39			
3	642.79	497.50	-.58025	1.000
5	642.79			
4	681.39	507.10	.26462	.7962
5	642.79			

Table 17: Results of T-test (Wet-Ashed Bone)

Ten Elements				
Group	Mean	Std Dev	T-Stat	Signif
1	107.98	91.315	-2.0321	.0727
2	166.66			
1	107.98	45.607	-1.230	.2499
3	125.72			
1	107.98	39.274	-2.1941	.0559
4	135.23			
1	107.98	159.05	-.50435	.6261
5	133.35			
2	166.66	55.056	2.3515	.0432
3	125.72			
2	166.66	58.632	1.6952	.1243
4	135.23			
2	166.66	156.67	.67241	.5182
5	133.35			
3	125.72	34.001	-.88449	.3994
4	135.23			
3	125.72	132.0	-.1827	.8591
5	133.35			
4	135.23	164.26	.36269	.9719
5	133.35			

Table 18: Results of Pairwise Rank Test (Wet-Ashed Bone)

Group	Twelve Elements	Ten Elements
	Significance	Significance
1 2	.3877	.1094
1 3	.1460	.3438
1 4	.3877	.1094
1 5	.7744	.7539
2 3	.0063	.0020
2 4	.7744	1.000
2 5	.7744	.7539
3 4	.0063	.0215
3 5	.7744	.7539
4 5	.7744	.7539

Table 19: Results of r correlations of group data (Wet-Ashed)

Twelve Elements

R @ .05 = .5760 R@ .01 = .7079

Group 1	1.0000				
Group 2	.9904	1.0000			
Group 3	.9963	.9983	1.0000		
Group 4	.9976	.9974	.9995	1.0000	
Group 5	.9421	.9008	.9195	.9210	1.0000
	Group 1	Group 2	Group 3	Group 4	Group 5

Table 20: Results of r correlations of group data (Wet-Ashed)

Ten Elements

	R@.05=.6319		R@.01=.7646		
Group 1	1.0000				
Group 2	.8951	1.0000			
Group 3	.9738	.9593	1.0000		
Group 4	.9577	.9750	.9800	1.0000	
Group 5	.9092	.8016	.9229	.8362	1.0000
	Group 1	Group 2	Group 3	Group 4	Group 5

Table 21: Rank Order Correlations (Wet-Ashed Bone)

Twelve Elements

Groups	Tau	Signif.	Rho
1 and 2	.8788	.0000	.9441
1 and 3	.9091	.0000	.9720
1 and 4	.9091	.0000	.9720
1 and 5	.7879	.0001	.9231
2 and 3	.9697	.0000	.9930
2 and 4	.9697	.0000	.9930
2 and 5	.6667	.0018	.8531
3 and 4	1.0000	.0000	1.0000
3 and 5	.6970	.0010	.8811
4 and 5	.6970	.0010	.8811

Table 22: Rank Order Correlations (Wet-Ashed Bone)

Ten Elements

Groups	Tau	Signif.	Rho
1 and 2	.8222	.0004	.9030
1 and 3	.8667	.0001	.9515
1 and 4	.8667	.0001	.9515
1 and 5	.7333	.0022	.8788
2 and 3	.9556	.0000	.9879
2 and 4	.9556	.0000	.9879
2 and 5	.5556	.0288	.7576
3 and 4	1.0000	.0000	1.0000
3 and 5	.6000	.0167	.8061
4 and 5	.6000	.0167	.8061

Table 23: Results of T-test (Dry-Ashed Bone)

Eleven Elements				
Group	Mean	Std Dev	T-Stat	Signif
1	1224.5	322.37	.24301	.8111
2	1205.5			
1	1224.5	319.85	2.7754	.0135
3	1009.2			
1	1224.5	194.2	-.10427	.9183
4	1229.4			
1	1224.5	1354.0	.12288	.9037
5	1184.1			
2	1205.5	335.84	2.4100	.0283
3	1009.2			
2	1205.5	244.10	-.40389	.6916
4	1229.4			
2	1205.5	1386.0	.63521	.9501
5	1184.1			
3	1009.2	326.94	-2.772	.0135
4	1229.4			
3	1009.2	1247.1	-.57841	.5710
5	1184.1			
4	1229.4	1393.8	.13390	.8952
5	1184.1			

Table 24: Results of T-test (Dry-Ashed Bone)

Eight Elements				
Group	Mean	Std Dev	T-Stat	Signif
1	2204.3	369.15	-.56277	.5912
2	2277.8			
1	2204.3	222.22	.87710	.4095
3	2135.4			
1	2204.3	283.77	-.53064	.9592
4	2209.6			
1	2204.3	1947.3	-.43984	.6733
5	2507.1			
2	2277.8	459.26	.87676	.4097
3	2135.4			
2	2277.8	237.91	.80992	.4446
4	2209.6			
2	2277.8	2052.3	-.31612	.7611
5	2507.1			
3	2135.4	272.08	-.77174	.4655
4	2209.6			
3	2135.4	1863.1	-.56435	.5901
5	2507.1			
4	2209.6	-297.50	-.41776	.6886
5	2507.1			

Table 25: Results of Pairwise Rank Test (Dry-Ashed Bone)

Group	Eleven Elements	Eight Elements
	Significance	Significance
1	.8036	.0703
2		
1	.0074	.2891
3		
1	.3323	.2891
4		
1	.1185	.7266
5		
2	.0213	.2891
3		
2	.4545	.2891
4		
2	.0768	.7266
5		
3	.0023	.2891
4		
3	.5488	.7266
5		
4	.0490	.7266
5		

Table 26: Results of r correlations of group data (Dry-Ashed)

Eleven Elements

	R @ .05 = .7067		R @ .01 = .8343		
Group 1	1.0000				
Group 2	.9888	1.0000			
Group 3	.9959	.9827	1.0000		
Group 4	.9933	.9954	.9938	1.0000	
Group 5	.7224	.6921	.7456	.7015	1.0000
	Group 1	Group 2	Group 3	Group 4	Group 5

Table 27: Results of r correlations of group data (Dry-Ashed)

Eight Elements

 $R_{.05} = .7067$ $R_{.01} = .8343$

Group 1	1.0000				
Group 2	.9832	1.0000			
Group 3	.9959	.9731	1.0000		
Group 4	.9933	.9902	.9938	1.0000	
Group 5	.7224	.6620	.7456	.7015	1.0000
	Group 1	Group 2	Group 3	Group 4	Group 5

Table 28: Rank Order Correlations (Dry-Ashed Bone)

Eleven Elements

Groups	Tau	Signif	Rho
1 and 2	.9542	.0000	.9886
1 and 3	.9630	.0000	.9909
1 and 4	.9175	.0000	.9749
1 and 5	.8889	.0000	.9635
2 and 3	.9175	.0000	.9795
2 and 4	.9273	.0000	.9727
2 and 5	.8441	.0001	.9522
3 and 4	.8808	.0000	.9658
3 and 5	.9259	.0000	.9726
4 and 5	.8074	.0002	.9385

Table 29: Rank Order Correlations (Dry-Ashed Bone)

Eight Elements

Groups	Tau	Signif.	Rho
1 and 2	.9286	.0004	.9762
1 and 3	.9286	.0004	.9762
1 and 4	.9286	.0004	.9762
1 and 5	.7857	.0055	.9048
2 and 3	.8571	.0017	.9524
2 and 4	1.0000	.0000	1.0000
2 and 5	.7143	.0141	.8810
3 and 4	.8571	.0017	.9524
3 and 5	.8571	.0017	.9286
4 and 5	.7143	.0141	.8810